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(54) METHOD FOR INHIBITING CORROSION IN HIGH TEMPERATURE, HIGH PRESSURE GAS WELLS

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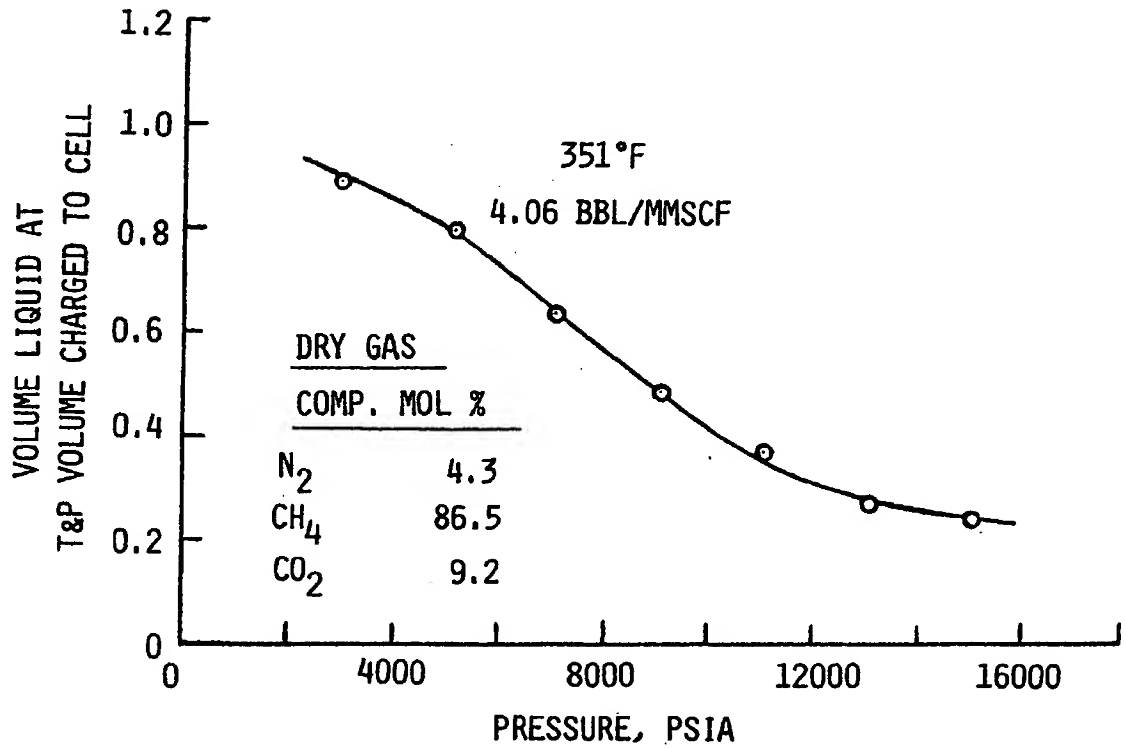
VOLUME FACTORS FOR DUOMEEN® T



METHOD FOR INHIBITING CORROSION IN HIGH TEMPERATURE, HIGH PRESSURE GAS WELLS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an improved corrosion inhibitor system for use in high temperature, high pressure gas wells. More specifically, it is concerned with a fatty amine optionally containing an oil soluble corrosion inhibitor which is capable of maintaining a protective film at high temperature, high pressure bottomhole conditions in the absence of a petroleum condensate phase.

2. Description of Prior Art

The utilization of chemical corrosion inhibitors to protect metal surfaces in various stages of oil and gas production has long been recognized as a necessary feature of oil and gas production. During the past half century, multitudes of chemical corrosion systems and methods of using them have been developed and have led to a vast number of patents and technical literature references. Thus, today corrosion engineering is considered an integral part of the planning and operation of virtually every stage of oil and gas production.

With ever increasing world energy demands and the advent of international fuel shortages, the oil and gas industry has been forced to drill deeper and deeper into more hostile environments in search of the critically needed fuel. As a result, certain high temperature, high pressure, deep horizon gas fields have been discovered throughout the world which present a severe challenge to

contemporary corrosion technology when one attempts to produce large volumes of natural gas in these fields.

The gas wells of particular interest in the present invention are characterized by a combination of properties that lead to corrosion rates manyfold higher than experienced in other gas fields. First and foremost, the gas wells are completed at great depths which in many cases exceed 20,000 ft. Consequently, the gas wells are categorically high temperature, high pressure wells. As a general rule, at bottomhole temperatures in excess of 250°F and bottomhole pressures of the order of about 4,000 psi, one can anticipate severe corrosion. As these bottomhole temperatures and pressures increase, the problems become even more pronounced such that at 400°F and pressures in excess of 5000 psi, the use of many corrosion inhibiting systems and methods is virtually prohibited. The gas wells of interest in the present invention are of this nature.

Furthermore, the particular gas wells of interest are dry wells in the sense that no liquid petroleum phase exists at the bottomhole conditions. Thus, no protective oil film will be present to coat the casing and to act as a corrosion inhibitor carrier. In fact, since no condensate phase exists at these bottomhole conditions, injection of oil-soluble inhibitors in a petroleum condensate carrier will be ineffective because of premature vaporization of the carrier before reaching the bottom of the well. To further complicate the lack of petroleum condensate phase at the bottomhole conditions, the gas wells of interest will have an aqueous or brine phase present, and this, in combination with acid gases such as hydrogen sulfide, carbon dioxide or the like, creates an extremely corrosive environment. With gas production in terms of tens of millions of standard cubic feet per day, the possibility of maintaining an oil condensate phase at bottomhole conditions is for all pragmatic purposes ruled out.

In an article entitled "Deep Wells - A Corrosion Engineering Challenge", by R. N. Tuttle and T. W. Hamby, presented at the International Corrosion Forum, April 14-18, 1975, held at Toronto, Ontario, it was acknowledged that recent emphasis on deep high temperature, high pressure horizons as potential gas producers and the associated hostile environments encountered presents a severe challenge to contemporary technology. In the article, it was pointed out that the bottomhole temperatures as high as 550°F have been encountered in south Texas, and bottomhole pressures exceeding 22,000 psi are present in Mississippi. It was also pointed out that tubing failure caused by corrosion in deep wells has been experienced in as little as eighteen months in the Lacq Field in France, Germany, Austria, and also Mississippi. The Thomasville-Piney Woods Field near Jackson, Mississippi, is exemplified as involving gas wells that fit the above description and have severe corrosion problems. The False River Field in Louisiana is believed to contain gas wells that would have bottomhole conditions characteristic of the present invention. The article concludes with the admission that a new corrosion inhibiting system to cover flowing conditions in the range of 18,000-20,000 psi and 380-450°F is needed for operation of anticipated future wells in south Texas and Mississippi.

SUMMARY OF THE INVENTION

In view of the severe corrosion problems encountered in gas wells producing from very deep high pressure and high temperature horizons wherein no petroleum condensate phase exists at bottomhole but an aqueous or brine phase can be present, we have developed a method for inhibiting corrosion in such wells involving the step of:

Injecting an effective amount of a high molecular weight fatty amine having from about 12 to 30 carbon atoms into said gas well thus producing a protective film forming phase at bottomhole conditions.

In one aspect of the invention, the fatty amine is injected into the bottom of the gas well by itself. In

another aspect, a small but effective amount of an oil soluble or oil compatible corrosion inhibitor is added to the film forming fatty amine carrier prior to injection into the gas well. Thus, the primary objective of the present invention is to provide a film forming liquid phase which is compatible with conventional oil base corrosion inhibitors such that injection of small volumes of the liquid into the gas wells wherein a petroleum condensate phase does not exist will result in a protective corrosion inhibiting liquid phase downhole. In other words, the primary objective of the present invention is to provide an alternate corrosion inhibitor carrier that will perform in high temperature, high pressure gas wells without condensate in a manner analogous to the performance of an oil condensate/inhibitor system in a gas well containing a liquid petroleum phase.

BRIEF DESCRIPTION OF THE DRAWING

The DRAWING illustrates the volume factor as a function of pressure for the N-alkyl-1,3-propane diamine mixture (sold as Duomeen T) in presence of dry gas at 350°F.

THE DESCRIPTION OF THE PREFERRED EMBODIMENTS

Upon recognition of the severe corrosion problems associated with the aforementioned types of gas wells and the realization that the lack of a protective film forming condensate phase at bottomhole conditions is the cause of the problems, only a limited number of alternatives are available aside from capping the well and stopping production. Each of these alternatives is in some way less than fully acceptable. Since there is an aqueous phase present at bottomhole conditions, the use of a water soluble corrosion inhibitor is one alternative. However, the protective film forming characteristics of a aqueous phase is acknowledged as inferior to that of an oil film and in combination with high gas flow rates, characteristically in excess of 10 MMSCFD (million standard cubic feet per day), makes the use of a water corrosion inhibitor system ineffective. Since the oil condensate

another aspect, a small but effective amount of an oil soluble or oil compatible corrosion inhibitor is added to the film forming fatty amine carrier prior to injection into the gas well. Thus, the primary objective of the present invention is to provide a film forming liquid phase which is compatible with conventional oil base corrosion inhibitors such that injection of small volumes of the liquid into the gas wells wherein a petroleum condensate phase does not exist will result in a protective corrosion inhibiting liquid phase downhole. In other words, the primary objective of the present invention is to provide an alternate corrosion inhibitor carrier that will perform in high temperature, high pressure gas wells without condensate in a manner analogous to the performance of an oil condensate/inhibitor system in a gas well containing a liquid petroleum phase.

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phase is nonexistent at bottomhole conditions, conventional addition of an oil soluble corrosion inhibitor dissolved in an oil carrier is virtually impossible. However, overdisplacing the gas well with large volumes of oil containing an oil based inhibitor is an alternative. Such an alternative is expensive in that very large volumes are required which in turn reduce gas production rate and require expensive oversized equipment to achieve the necessary injection rates. Less volatile heavy oils have been employed in the overdisplacement technique to partially offset the extremely large volumes. It has also been suggested that more expensive, exotic, noncorrosive metals be employed. And more frequent pulling and replacing of production tubing has been implemented. As of now, none of the alternatives or combinations of the alternatives have proven to be equivalent of what would be expected if an oil condensate phase could be maintained at bottomhole conditions. The previously referenced R. N. Tuttle, et al., article summarizes an ideal solution to the problem in the following way, "A simplier approach would be to use a heavy oil which would provide a high dew-point pressure at low concentrations in the mixed gas/oil inhibitor phase (if one can be found)."

The present invention is such a system. We have discovered that high molecular weight fatty amines are capable of existing in a liquid phase at bottomhole conditions characteristic of the dry gas wells of interest. This liquid phase is found to be an effective corrosion inhibitor as well as an effective oil base corrosion inhibitor carrier with excellent film forming properties. Thus, such compositions are extremely useful in suppressing corrosion in the very hostile environments of interest. Accordingly, a liquid phase has been observed at high temperatures and high pressures in the presence of what corresponds to high gas flow rates even though relatively small quantities of corrosion inhibiting compositions were employed.

By far the most important feature of the present invention relative to what has previously been employed is that the compositions in the prior art are incapable of sustaining a liquid phase at the conditions characteristic of the gas wells of interest, whereas the compositions of the present invention do exist in a liquid phase under the same hostile conditions. This phase behavior difference is a consequence of the compositional distinctions involved in selecting the fatty amine.

The high molecular weight fatty amines used in the present invention are, in principle, long chain alkyl amines usually synthesized from naturally occurring fatty acids wherein the alkyl groups involved have an average length in excess of twelve carbon atoms. Commercially available fatty amines will usually contain mixtures of alkyl chain lengths since they are derived from fatty acids occurring in nature. Frequently, this will also result in an abundance of the even carbon number species and the presence of unsaturation such as found in the oleic, palmitic, and the like structures. However, any long chain predominately aliphatic amine, whether it be a single species with either even or odd numbered carbon atoms or mixtures of these species, is viewed as an acceptable high molecular weight amine for the purposes of this invention. These fatty amines are preferably waxy solids or semi-solids which are easily melted at temperatures characteristic of the gas wells of interest. The preferred amines will involve carbon chain lengths of 16-30 carbon atoms. This preferred range is consistent with the present view that increasing the molecular weight in order to decrease the volatility is of paramount importance in achieving the desired liquid phase at bottomhole high temperatures and high pressures. A preferred subclass of fatty amines which have been found to be particularly useful in the present invention is the N-alkyl-1,3-propane diamines. For a more complete discussion of the high molecular weight aliphatic amines, their respective chemical identities, commercial sources, physical and chemical

properties, known uses, and m thods of synthesis, the FATTY AMINES chapter starting on page 283 of the 3rd Edition, Volume 2, KIRK-OTHMER, "Encyclopedia of Chemical Technology" is pertinent.

It is felt that the presence of the liquid fatty amine phase in the presence of high flow rate gas at high temperatures and high pressures is critical to successful corrosion inhibition. In order to confirm the presence of the desired liquid phase at bottomhole conditions, a series of phase distribution measurements in a variable volume window PVT cell were performed.

The particular fatty amine employed in the testing was a mixture of N-alkyl-1,3-propane diamines having an average carbon number of 18 supplied by Armak of Chicago under the trade name Duomeen* T. This fatty amine is described as a N-tallow-1,3-propane diamine having the general formula, $RNHCH_2CH_2NH_2$. The compositional distribution of a typical mixture of alkyl radicals (the R in the above formula) and some typical properties of this fatty amine are presented in TABLE I.

*A trademark of Armour Industrial Chemical Company

TABLE II

Component	Mol Percent
Nitrogen	4.3
Methane	86.5
Carbon Dioxide	9.2

This particular composition corresponds to 4.06 barrels of fatty amine being injected into gas well per million standard cubic feet of gas being produced from the well (Bbl/MMSCF). The PVT cell was held at 351°F (177°C) while the volume was varied such that the pressure in the cell ranged from approximately 3,000 psia up to 15,000 psia. The total volume of the cell and the volume of the liquid phase present in the cell were recorded at the various pressures and are presented in TABLE III and the DRAWING.

TABLE III

Phase Distribution Test Results and Volume Factors for Duomeen T in a Mixture of 4.06 Bbl Duomeen T/MMSCF Gas(1) at 350°F

Pressure, psia	Total Volume(2), cc	Liquid Volume, cc	Volume % Liquid	Volume Liquid at T&P per Volume Duomeen T Charged
2976	1301.74	3.4	0.26	0.895
5103	811.99	3.0	0.37	0.789
7057	637.15	2.4	0.38	0.631
9061	543.27	1.8	0.33	0.474
11018	486.39	1.4	0.29	0.368
13080	445.50	1.0	0.22	0.263
15036	417.38	0.9	0.22	0.237

As indicated in the third and fourth columns of TABLE III, a significant amount of liquid phase was present throughout the entire pressure range at the tested conditions. This establishes that the critically needed liquid phase will exist at bottomhole conditions corresponding to the test conditions. The fifth column represents the ratio of volume of liquid at the specified temperature and pressure per volume of fatty amine injected. Such data are of practical importance for designing a commercial well treatment in that it quantitatively reflects

the relative volume of liquid phase remaining at various pressures (depths) in the well when 4.06 Bbls of fatty amines are injected per MMSCF of gas being produced. For example, at approximately 15,000 psi 23.7% of the volume injected is the volume of liquid phase at well conditions. This feature is further illustrated in the DRAWING where a continuous curve depicting the volume factor of Duomeen T from approximately 3,000 psia up to 15,000 psia establishes the presence of a critical liquid phase throughout the entire range. It is significant to note that the liquid phase is present even though the quantity being injected corresponds to approximately 4 Bbls/MMSCF of gas being produced. In contrast, it is not uncommon in extremely hostile downhole environments of interest to previously measure the amount of injected fluid in terms of hundreds of barrels per MMSCF. As such, the present invention accomplishes what the previously referenced R. N. Tuttle, et al., article described as an ideal solution to the problem. In doing so, the proposed method makes the volume of injected fluid essentially equivalent to what is conventionally employed in shallower wells wherein the bottomhole conditions are compatible with the presence of a liquid petroleum condensate phase. This means that the present invention can be implemented with equipment and procedures essentially identical to the less hostile oil and gas wells.

From the composite of the phase distribution data presented here, certain basic concepts relative to the practice of the present invention can be established. First and foremost the use of the fatty amine as a corrosion inhibitor or corrosion inhibitor carrier results in the presence of a liquid phase even under severe high temperatures and high pressures associated with the deep dry gas well of interest. Furthermore, significant volumes of liquid phase can be maintained at bottomhole conditions in the presence of very high rates of dry gas production with as little as 4 Bbls of injected oil/MMSCF of dry gas being produced. As previously stated, since the compositions of

the present invention achieve the desired liquid phase at very favorable low injection rates, they can be employed in a manner analogous to previous practices associated with inhibiting corrosion in gas wells wherein a condensate phase can exist at bottomhole conditions. Such methods include periodic or continuous injection of the corrosion inhibitor with or without a diluent and the like.

In addition to the presence of a liquid phase at these hostile bottomhole conditions, the fatty amines of the present invention inherently possess other advantageous properties. First, the fatty amines exhibit excellent film forming properties at high temperatures and pressures. This is viewed as being beneficial in surpressing corrosion in that good film forming properties result in more uniform coating of the exposed steel surfaces and optimizes corrosion inhibition. Secondly, the fatty amines exhibit corrosion inhibition in and of itself in a manner analogous to what is known with respect to organic amines when used at less severe temperatures and pressures. With regards to the corrosion inhibition property, the N-alkyl-1,3-propane diamines are again viewed as being the preferred fatty amine in that the presence of the second amine nitrogen enhances the corrosion inhibition.

In order to further enhance the corrosion inhibition properties of the fatty amine, an effective amount of an oil soluble or oil base corrosion inhibitor can be added prior to injection into the well. In this manner, the fatty amine is functioning as a corrosion inhibitor carrier similar to what is commonly practiced in the oil and gas production industry at lower pressures and temperatures wherein various oil condensates, diesel oil, and the like are used as carriers. Such a process involves the addition of an effective amount of the conventional oil soluble or so-called oil based corrosion inhibitor to the fatty amine and then injecting the mixture into the gas well to be treated. These oil soluble or oil based

corrosion inhibitors include, but are not limited to, such additives as organic polar and heteropolar compounds containing nitrogen, oxygen, sulfur, and/or other elements in Groups V and VI which include amines, amids, mercaptans, heterocyclic nitrogen compounds, ureas, thioureas, phosphates, polyphosphates, oxyalkylates, and the like. Again, the unique aspect of the use of the fatty amine as a corrosion inhibitor carrier involves the ability of fatty amine to sustain a liquid film forming phase at severe hostile conditions even when using very small volumes of injected fluid.

The actual injection of the corrosion inhibiting compositions of the present invention can be accomplished by any of the methods commonly practiced in the oil and gas industry for surpressing corrosion or adding additives to downhole fluids. Since the desired liquid phase can be achieved at relatively small volumes of injected fatty amines, the use of a spaghetti string injection system or the like is preferred.

Having thus described the preferred embodiments, the invention is not to be construed as limited to the particular forms disclosed and tests, since these are regarded as illustrative rather than restrictive. Therefore, the following claims are intended to cover all processes which do not depart from the spirit and scope of using in high temperature, high pressure wells, a relatively nonvolatile high molecular weight fatty amine as a corrosion inhibitor or corrosion inhibitor carrier.

WE CLAIM:

1. A method for inhibiting corrosion in a high temperature, high pressure gas well, characterized in that no petrol um condensate phase xists at bottomhol conditions, involving the step of: injecting an effective amount of a high molecular weight fatty amine, having from about 12 to 30 carbon atoms, into said gas well thus producing a protective film forming phase at bottomhole conditions.

2. A method for inhibiting corrosion according to Claim 1 wherein said fatty amine contains an oil soluble corrosion inhibitor.

3. A method for inhibiting corrosion according to Claim 1 wherein said fatty amine is a N-alkyl-1,3-propane diamine.

4. A method for inhibiting corrosion according to Claim 3 wherein the alkyl group contains from about 16 to 30 carbon atoms.

5. Method as in Claim 1 wherein the high temperature, high pressure gas is further characterized in that an aqueous or brine phase is present.

6. A method for inhibiting corrosion according to Claim 2 wherein said fatty amine is an N-alkyl-1,3-propane diamine.

7. A method for inhibiting corrosion according to Claim 6 wherein the alkyl group contains from about 16 to 30 carbon atoms.

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ABSTRACT OF THE DISCLOSURE

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A method for inhibiting corrosion in a high temperature, high pressure gas well in which an aqueous or brine phase is present but no petroleum condensate phase exists at bottomhole conditions, involving the injection of a relatively high molecular weight predominantly aliphatic amine (e.g., a fatty amine, particularly, the N-alkyl-1,3-propane diamine) into the gas well on its own or in combination with conventional oil based corrosion inhibitor additives to inhibit corrosion. Such a method is particularly useful in sustaining a liquid film forming phase at hostile bottomhole conditions.